An assessment of intrinsic noise of pseudo-reference electrodes and instrumental noise to enable reliable electrochemical noise measurements in situ on organically coated metal

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Abstract

Electrochemical noise measurement (ENM) is well-established as a standard test procedure for laboratory use to assist in assessing organic coatings. However, its non-destructive nature makes it particularly appealing for field use i.e. the monitoring of actual structures. A fundamental requirement for collecting valid electrochemical noise data in any situation is the use of a stable reference electrode that produces as little noise as possible. This is particularly important for organically coated substrates, where the currents being measured are very small due to attenuation of the signal by the high-impedance coating. Standard electrodes, e.g. the saturated calomel electrode, are not suitable for field measurements. In the present study, a method of assessing candidate electrodes and their noise characteristics is proposed leading to a suggestion for a suitable pseudo-reference electrode (PRE). An important conclusion is that when used as a PRE, the area of the electrode influences the noise characteristics. In general, the smaller the electrode the lower the current noise. But this has to be balanced against small electrodes having higher impedance, the latter being undesirable, so an optimization is needed.

Keywords

Electrochemical noise measurement; pseudo reference electrode; in situ testing; intrinsic noise; instrument noise

1. INTRODUCTION

1.1 Background on ENM

Electrochemical noise measurement (ENM) is a non-destructive test method with unique capabilities for studying corrosion behaviour, e.g. localized attack on metal, general corrosion rate of metal and the protective performance of surface coatings. The method relies on the simultaneous recording of current and potential fluctuations generated by the corroding electrodes in the absence of an external voltage or current source; hence, the measurement is non-destructive. The application of ENM to bare metal has been well-documented and is standardised in ASTM G199 - 09(2014) and ISO 17093:2015. The latter standard contains an Appendix on application of noise to assess paint coatings and this is complimented by a technical specification (ISO //TS 5604) currently in preparation. The normal method of making noise measurements (the so-called "salt bridge" electrode configuration (see Figure 1a) requires two electrically isolated working electrodes (WEs), e.g. corroding samples or coated panels, and a low-noise reference electrode (RE). The current flow between the two WEs is measured simultaneously with the potential fluctuation between the WEs and the RE. When making measurements on coated substrates in the field Pseudo Reference electrodes (PREs) may be used in place of standard laboratory reference electrodes [1,2]. These do not have an ionic junction and the potential generated will depend on the concentration of chloride (in Ag/AgCl) or sulphate (in $Cu/CuSO_4$) or oxygen (Pt) that they are in contact with. However, as long as that concentration remains constant the electrode potential of the PRE will remain constant. When it comes to examining paint coatings there are two other factors: the impedance of the system is higher and therefore the measured noise levels are lower so the level of potential noise arising in the reference electrode becomes important [3]. And secondly in practical field arrangements of ENM both the low voltage noise and low current noise of the PRE will be critical.

Figure 1

1.2 ENM arrangements for measurements on organically coated metal substrates in the field

The necessity of two electrically isolated WEs prevents the standard ENM arrangement (salt bridge in Fig. 1) being easily applicable in the field. For example, it is impossible to find two

identical and isolated bridges, pipelines, or ships in close proximity to use each as an individual WE. Therefore, two other electrode arrangements have been advanced in recent years to allow the measurement to be conducted on a single coated object. These are named Single Substrate (SS) [4,5] and No Connection to the Substrate (NOCS) [6], schematically represented in Figures 1b and 1c, respectively. A brief review of these can be found in reference [7] and further investigation and validation of these electrode arrangements can be found in references [5,6,8–10] for SS arrangement and in [1,6,11–17] for the NOCS. The SS arrangement has also been extensively implemented for corrosion measurements using embedded electrodes due to its practicality [18–23]. While these arrangements resolve the issue of the need for two electrically isolated test subjects, they effectively place the reference electrode within the electrical circuit with the ZRA that is measuring the current noise as well as the potentiometer measuring the potential noise. Figure 2 shows the equivalent electrical circuit for salt bridge (Figure 2a) [24] and the SS electrode arrangements (Figure 2b) [10]. Therefore, in addition to being sensitive to the voltage noise arising from the reference electrodes, the SS and NOCS arrangements are also sensitive to their current noise.

The other factor is impedance of the reference electrode. It is important that this is kept as low as possible for a valid and meaningful electrochemical noise measurement [5,10]. This has also been demonstrated for other DC and AC electrochemical test methods [25–34]. In particular, in the case of ENM with SS electrode configuration it was shown that the impedance of reference electrode adds to the overall noise resistance, R_n, and this would present a serious issue if a relatively high impedance electrode is used for assessing poorly coated or bare metals [10].

Figure 2

1.3. *Measuring sources of noise not originating from the sample under investigation*

While the study and measurement of instrumental noise against dummy cells have been extensively practiced in the published guidelines and literature [35–41], the importance of measuring intrinsic noise of the reference electrode seems to have been neglected. The majority of theoretical studies on the analysis of electrochemical noise signal have tended to assume that the reference electrode is "quiet enough" [10,24,42]. In reality, all redox reference electrodes generate levels of intrinsic noise. This voltage and current instability

become more pronounced when it comes to pseudo-reference electrodes (PREs) where the ion concentration participating in the reversible redox reactions cannot be precisely controlled. In some cases, simple platinum or silver or Ag/AgCl wires served as pseudo- or quasi-reference electrodes. Obviously, thermodynamic equilibrium cannot exist, since there is no common component (anion or cation) in the two adjacent phases [43].

1.4 *Challenges of on-Site measurement*

The application of the technique to remote site investigations such as studying corrosion performance of ships [44,45], environmental damage to public artwork [1], infrastructure paint coating [2], and microbiologically induced corrosion (MIC) in marine environment [46,47], has introduced additional challenges. These have been met in various ways as illustrated in Figure 3. One obstacle has been the lack of portable instrumentation. This has been overcome in the past by use of modem and telephone line for data communication from remote marine test sites as illustrated in Figure 3a [46,47] or the powerline extension and large battery packs as shown in Figures 3b and 3c. A recent development is the ProCoMeter (manufactured by DCVG ltd., UK) which is a specialized portable instrument for ENM enabling convenient utilization in the field [48–51]. Figure 3d and 3e exemplify the use of ProCoMeter for assessment of protective coating on Salt River Siphon water pipeline in Arizona (USA) [51] and Metal Cultural Artefacts at Maritime Museum of Gdansk (Poland) [52], respectively. The remaining obstacle in this area is to identify a near ideal reference electrode for field application that exhibits low levels of electrochemical potential and current noise as well as low impedance. PREs such as Ag/AgCl [50,51], Cu pad [1,2] have previously been implemented in field investigation using SS and NOCS arrangements but without taking into consideration the electrochemical current noise levels of the reference or pseudo reference electrode. This could explain some of the rather scattered results that have been obtained. Note it is known that silver/silver chloride electrodes are light sensitive, but this has not been a problem in this work where the PRE is placed within a sandwiched pad in contact with the coated surface and hence is effectively shielded from the light.

Figure 3

1.5 *Aim of present study*

The aim of the present study is to investigate the factors that could interfere with successful noise measurement for evaluation of organic coatings in the field. This paper starts by looking at instrument noise and moves on to investigate a range of pseudo-reference electrodes by measuring their impedance, potential noise and current noise levels. Finally model coatings are examined using the best PRE and values are compared to that acquired by other electrochemical methods in order to validate the results.

2. EXPERIMENTAL

2.1 Materials and instrumentation

2.1.1 ENM

ENM was performed using a ProCoMeter (DCVG, UK). The ProCoMeter has recently been developed as a specialised portable electrochemical noise data acquisition and analyser by DCVG ltd. for the assessment of paint coatings and corrosion protection in the field. The device is battery operated and therefore immune from powerline related systematic noise. The standard operation conveniently allows identification of the and selection of the proper internal resistor and autoranging is not implemented during the ENM in compliance with the published guidelines [36]. This is to eliminate the artefacts and systematic noise that is commonly observed due to the autozero and autoranging feature in potentiostats.

The accuracy of ProCoMeter is also examined using a calibration box (manufactured by DCVG ltd.) with built-in set current and voltage values (see Fig. S1 in supplementary materials).

EN data was treated using the appropriate integrated software supplied for the ProCoMeter. This software allows DC detrending using linear and polynomial (depending on the nature of data set) as well as frequency domain transformation using fast Fourier transform (FFT) function and calculations. Additionally, both software packages allow the data set to be "brushed". This latter involves visually selecting certain fraction of the data set for statistical analysis.

2.1.2 Instrumental Noise

The instrumental noise of ProCoMeter was measured using a dummy cell with star configuration (Fig. 4) consisting of three identical resistors according to the procedure outlined in reference [35,36,39]. Resistors were all 0.125W metal film type with 0.1% tolerance from Vishay Dale. Values were 1kΩ, 10kΩ, 100kΩ and 10MΩ. The high, medium and low resistor values are included to mimic an intact resistive coating, a damaged coating/resistive oxide film and an active metal surface, respectively.

Figure 4

Each set of data is comprised of 3072 data points at either 20Hz or 1Hz sampling frequency. 20Hz and 3072 are the highest sampling frequency and largest dataset (in one batch) that can be recorded by the ProCoMeter. The assessment of the instrumental noise is essentially performed in the frequency domain by comparing the measured potential and current PSDs to the thermal noise PSDs of the resistors.

2.1.3 Electrodes investigated

A wide range of electrode materials was investigated. The $Cu/CuSO_4$ (Fig. 5a) and Ag/AgCl (Fig. 5b) pseudo-reference electrodes were supplied by DCVG ltd. The Ag/AgCl electrodes were made from a mix of silver and silver chloride sintered to form a 2mm thick disc with total surface area of ~4.15 cm^2. Additional Ag/AgCl electrodes were also fabricated from silver rod (99.99% purity) with 2.1mm OD and the AgCl layer was formed by anodising in NaCl. The Cu foil (purchased from Goodfellow) used in the copper "pad" had 99.9% purity and ~3.2 cm^2 surface area. The saturated Calomel electrode, SCE, (Fig. 5c) was "R1 Reference Electrode" from SENTEK, UK, with a glass body, ceramic frit junction and 12mm OD. The platinum foil was from Goodfellow with 99.95 purity and 50μm thickness. Electrocardiogram (ECG) electrodes (Fig. 5d) were 3M™ Red Dot™ Solid Gel Electrode from 3M. The electrolytically conductive gel was Cross-linked guar gum. The sensor material was Silver/silver-chloride coated plastic. Gel area was ~2.54 cm^2 and the sensor diameter was ~0.5 cm^2. Carbon electrode was a solid graphite rod (Fig. 5e) with 7mm OD.

Figure 5

2.2 Procedure

2.2.1 Voltage stability test (VST)

Since PREs are not ideally nonpolarizable electrodes, there is often a shift of their potential during the measurements, depending on the current density (due to the voltage difference with the other electrode in circuit via ZRA) and ionic composition in the electrolyte [43]. In most cases the electrode's voltage drift can be removed (by detrending) from the measured EN data later using software packages but the voltage and/or current fluctuation from the electrode itself cannot be deconvoluted from the measured data once it is amalgamated with the electrochemical signal from the corroding test subject. It is therefore imperative to ensure that the intrinsic voltage and current noise levels of the electrodes are sufficiently low so that the contribution of the reference electrode to the total ENM is negligible.

The Voltage Stability Test (VST) was performed using the ProCoMeter according to the set-up shown in Figure 6a. The VST was conducted for each individual pseudo-reference electrode either Cu /CuSO$_4$ or Ag/AgCl by measuring the voltage against a standard SCE (Figure 5c) in an appropriate solution for steady state potential (e.g. for Cu in 5%wt. CuSO$_4$, and for Ag/AgCl in 3%wt. NaCl). A total of 3072 data points were gathered at 0.5 sec intervals (i.e. 2Hz). The procedure was repeated several times for each individual electrode. The difference between the highest and lowest voltage values is reported as the measure of DC drift during the experiment. An appropriate de-trend function (in most cases quadratic polynomial, i.e. n=2) was applied to the graph from each run to calculate standard deviation of voltage (σE). The latter is taken to be the voltage noise of the electrode under investigation. To check that the Calomel itself has a very small voltage noise, the value obtained when both electrodes were Calomels was measured. This was found to be less that the voltage noise of any of the other electrodes.

2.2.2 Current noise and impedance

The VST above examined electrodes individually. In the Single Substrate and NOCS arrangements of ENM, either two (in SS) or three (in NOCS) PREs are used in combination (see Fig. 1). Hence the current noise level of the PRE becomes important. Also, another critical parameter for a good PRE, apart from high voltage stability and low noise, is low

impedance. The noise characteristics were examined using three nominally identical electrodes of the same kind as the WEs and RE in the experimental setup shown in Figure 6b. The current and voltage noise of a range of different electrodes were measured in contact with 3% NaCl inside a Faraday cage for 512 s with a 0.5 s sampling frequency (i.e. 2Hz). A 30 min settle time was allowed prior to commencing data acquisition. The 30 min settle time was chosen as suggested by the VST test results (see section 3.2). This settle time is also the recommended time-to-equilibrium for the testing of typical polymer coatings. The impedance was also measured using EIS technique with Reference 600 (Gamry, USA) in a standard three electrodes configuration.

Figure 6

3. RESULTS AND DISCUSSION

3.1 Instrumental noise

The power spectral density (PSD) of the thermal noise is calculated as 6 kTR for the potential thermal noise and 2kT/R for the current [53] with k=1.38×10^{-23} J/K and T=298 °K. These theoretical values are tabulated in Table 1. Figures 7-10 show the time record along with the experimental PSD and its comparison to the theoretical PSD of the thermal noise for each individual resistor. Theoretical values of thermal noise are shown as a broken line in the PSD plots.

Table 1. PSD values of potential and current thermal noise for the resistors used in the dummy cells (potential thermal noise as 6 kTR and current thermal noise as 2 kT/R with k=1.38×10^{-23} J/K and T=298 °K).

	Resistor values (Ω)			
	R=10^3	R=10^4	R=10^5	R=10^7
Potential thermal noise PSDs (V^2 Hz^{-1})	2.42×10^{-17}	2.42×10^{-16}	2.42×10^{-15}	2.42×10^{-13}
Current thermal noise PSDs (A^2 Hz^{-1})	8.08×10^{-24}	8.08×10^{-25}	8.08×10^{-26}	8.08×10^{-28}

Figure 7

Figure 8

Figure 9

Figure 10

The time record shows proper resolution with no sign of quantisation even at fA level in the case of 10MΩ resistor (Figures 7&8). The assessment of the instrumental noise is essentially performed in the frequency domain by comparing the measured potential and current PSDs to the thermal noise PSDs of the resistors. The baseline noise of the equipment depends on the resistance through the circuit, so it should be measured for different resistors [35]. The potential noise arises from the application of the current noise on the impedance of the system. This effect is clearly seen in the results (Figures 7-10 and Figures S2-S5) as the potential noise level is amplified by the larger resistor while the current noise is attenuated.

Comparing to the previously published results of a round-robin study [36] on a large number of commercial instruments, the noise level generated by the ProCoMeter is in an acceptable range and significantly lower than the typical noise that is generated by the real-life electrochemical corrosion systems. The instrument uses a digital adaptive filtering system that appears to generate a systematic noise with 4Hz bandwidth when sampled at 20Hz. This is apparent from the sharp peak in both of the current and voltage PSDs in Figures 8 and 10. The fall in the PSD of current and potential, in particular in the case of 20Hz data acquisition, suggests the presence of anti-aliasing filter [35,36,39] although the filter in this case would not be operating on the powerline frequency (e.g. 50Hz or 60Hz) as the device is battery operated.

The sampling frequency at which the following results are generated is 2Hz. At this sampling frequency the PSD plots did not exhibit signs of systematic instrumental noise (figures 7 and 9). This ensures that the data was unaffected by systematic instrumental noise. For more context regarding filtering mechanism by Procometer see supporting materials.

3.2 Voltage stability test (VST)

Table 2 summarises VST results for four Ag/AgCl electrodes, four copper electrodes, four platinum electrodes, four graphite electrodes and two ECG electrodes in 3% NaCl. This table provides not only the voltage drift but also the voltage noise of each electrode and the average voltage of the electrodes on the Calomel scale. Figures 11 and 12 provide examples of the VST results for Ag/AgCl and Cu disc electrodes, respectively. The data presented in Figure 11 corresponds to the value reported as AgCl-2/2 in Table 2 showing 0.31mV drift of the voltage during ~27 min (i.e. 3072 data points at 2Hz sampling frequency) of measurement. Note that in the majority of field-work for painted metal items, 512 data points at 2Hz sampling frequency is typically collected. This empirical guideline is based on the fact that the paint coated metal test subjects are generally more stationary compared to the bare metal. Figures 11c and 11d are the magnified first 512 data points from Figures 11a and 11b. These show a stochastic noise characteristic without any sign of voltage transients. Figure 12 corresponds to the value obtained from Cu-2/1 demonstrating a DC voltage drift of 1.31mV over ~27 min (i.e. 3072 data points at 2Hz sampling frequency) of voltage measurement. PSD plots of voltage data presented in Figures 11 and 12 are provided in supplementary materials, Figures S9 and S10.

Table 2 Results of VST for all PREs as the value of DC drift over the measurement time (~27 min), standard deviation and mean value of voltage. Exposed electrode surface areas are given in experimental section. Surface area of graphite electrode was 3.2cm^2.

Electrode#/Run#	AgCl-1/1	AgCl-1/2	AgCl-2/1	AgCl-2/2	Cu-1/1	Cu-1/2	Cu-2/1	Cu-2/2
DC drift / mV	2.06	0.72	0.48	0.31	0.44	0.34	1.31	0.79
σE / μV	1.49	3.12	3.15	2.66	4.97	5.1	7.08	7.2
Average voltage / mV (vs. SCE)	5.07	11.3	10.7	10.3	40.5	40.05	28.41	29.19

Electrode#/Run#	C-1/1	C-1/2	C-2/1	C-2/2	Pt-1/1	Pt-1/2	Pt-2/1	Pt-2/2	ECG-1/1	ECG-1/2
DC drift / mV	15.91	14.99	3.93	2.46	7.35	5.54	3.18	2.86	2.38	0.61
σE / μV	5.11	5.16	5.18	5.2	4.15	5.11	7.3	5.3	2.66	2.56

| Average voltage / V (vs. SCE) | 207.55 | 191.66 | 165.44 | 162.18 | 122.65 | 129.58 | 137.96 | 141.24 | 4.37 | 5.77 |

- AgCl: Ag/AgCl
- C: graphite

Figure 11

Figure 12

In general, it was observed that the DC drift became smaller and the voltage graph plateaued as the immersion time increased. In all cases, the DC drift for Ag/AgCl and Cu PREs fell under 1mV after 30min immersion. It is also noteworthy that a similar time frame is typically required as a time-to-equilibrium for polymer coatings to absorb water and ions, and to form relatively stable electrolytically conductive pathways that allows an electrochemical measurement (including ENM) to be conducted and hence an accurate value of R_n to be obtained. A previous study on the time-to-equilibrium has demonstrated an exponential relationship between coatings' ionic resistance and exposure time in NaCl electrolyte with the resistance plateauing after almost 30min [2]. It is therefore strongly recommended that in any fieldwork at least 30min equilibrium time is allowed so that both the polymer coating and the PRE can arrive at an acceptable stationary state.

A number of additional Ag/AgCl (4.15 cm^2) and Cu (3.2 cm^2) electrodes were also examined. The results for three silver electrodes and two copper electrodes are given in table S1 in supplementary materials. These results show good reproducibility among the two copper electrodes and among the three silver electrodes. There is more drift (difference between 1st and 2nd run) on the copper electrodes than the silver electrodes. The voltage noise values on the second run from the silver electrodes are all very low (10-20μV). The copper electrodes produce significantly higher voltage noise (V_n).

Regarding the difference between $Cu/CuSO_4$ and Ag/AgCl, the conclusion from the results given in the Table 2 (as well as data in Fig 13) is that, although both types are comparable in terms of drift, and give reproducible values of voltage, the silver/silver chloride electrode is superior to the copper/copper sulphate in that it generates a considerably lower level of voltage noise.

3.3 Results for voltage Noise, current Noise and impedance characteristics of PREs

The following electrodes were investigated: a laboratory standard saturated Calomel electrode (SCE); graphite (C); electrocardiogram (ECG); Ag/AgCl solid state electrode; platinum (Pt); copper (Cu); and stainless steel(SS). Figure 13 presents a comparison of the noise characteristics in the form of current and potential standard deviations. The surface area was varied in the case of Pt, Cu and stainless steel and, as demonstrated by the results in Figure 13, the noise level increased significantly with increasing electrode surface area in all three cases. A sample of the data in the time domain (after DC trend removal), obtained from measuring the noise characteristics of electrocardiogram (ECG) electrodes, is given in Figure S11.

Figure 13

Theoretical analysis predicts that the current noise power is proportional to the specimen area, whereas the potential noise power is inversely proportional to the area [3]. The theoretical analysis also suggests a constant relationship between current and potential in a way that renders an inverse relationship between the specimen area and noise resistance [53]. Cottis [3,53] however draws attention to the fact that these assumptions are merely based on theoretical analysis and not systematic experimental studies which is lacking in this area. The current noise is considered to be produced by a large number of independent and uncorrelated current sources, e.g. pitting events, cathodic reactions etc, while the potential noise arises from the application of the current noise on the impedance of the system [24,42]. Therefore, since the power of the uncorrelated current noise from the various regions of the electrode will add together, the variance of the current noise, i.e., σI^2, is proportional to area. Hence, the amplitude of the current noise (measured as the σI) is proportional to $\sqrt{area}$ while the amplitude of the potential noise is proportional to $1/\sqrt{area}$ [7,55,56]. The current noise power is proportional to the surface area of the sample and therefore when two samples of the same size connect, the standard deviation of current noise will increase by $\sqrt{2}$. On the other hand, potential noise power is inversely proportional to surface area so the standard deviation of potential noise will reduce by a factor of $\sqrt{2}$. The same principle also applies to increasing the surface area of each sample, e.g., increasing the size of the sample ten times will increase

the current noise by $\sqrt{10}$ and will reduce the potential noise by a factor of $\sqrt{10}$ so the Rn should reduce 10 times. Thus, this is expected to result in the usual effect of changing the area on electrochemical measurements such as what is performed by EIS or PDP.

While the above exact mathematical relationship was not observed in the results presented in Figure 13, the σI data followed a similar trend. For example, the σI generated by Cu electrodes was reduced by about two orders of magnitude when the electrode surface area was reduced from $3.14 cm^2$ down to $0.07 cm^2$. Similar trend was observed for SS and Ag/AgCl PREs. One common observation was that the impact of surface area on the σI generally exceeds the mathematically predicted value. For example, reducing the size of Ag/AgCl electrode from $3.8 cm^2$ to $0.035 cm^2$ (100 folds) has decreased the σI by approximately four orders of magnitude. Similarly for the Pt electrode, the σI was decreased by about five orders of magnitude when the surface area was reduced from $2 cm^2$ to $0.03 cm^2$. The σE did not follow the mathematical model.

Although the current noise level is relatively high even in the case of a laboratory standard calomel electrode, it is worth noting that in practice, when measuring electrochemical noise for high impedance specimens (e.g. highly protective barrier coatings), the current is attenuated by the high impedance in the circuit. This could allow the use of reference electrodes such as calomel without significant impact on the results. However, when measuring systems with low levels of current noise and with relatively low impedance (e.g. passivated metal surfaces), this could introduce a significant source of error. It is therefore recommended to use electrodes with inherently low levels of both current and potential noise when it is suspected that the system being investigated has a low impedance.

In addition to the intrinsic noise generated by the pseudo-reference electrode, a third criterion for a reliable electrode for electrochemical noise measurement in the SS and NOCS arrangement is the low impedance of the electrode itself. A recent study [10] showed that, in the single substrate electrode arrangement, the impedance of the reference electrodes is added to the sum of resistances that are measured and calculated as the noise resistance according to equation 1:

$$R_n = \frac{R_{sol}}{2} + \frac{Z_{ref.1} + Z_{ref.2}}{2} + Z_{film} + Z_{m-s} \tag{1}$$

where R_{sol} is the solution resistance, $Z_{ref.1}$ and $Z_{ref.2}$ are the reference electrode impedance values, Z_{film} is the impedance of the organic coating and the Z_{m-s} is the impedance at the metal/solution interface. Therefore, it is also important to measure the impedance values of

the candidate pseudo-reference electrodes and ensure that the impedance level is not so high as to contribute a significant component to the measured noise resistance. EIS measurements were conducted using pseudo-reference electrodes both as working and counter electrodes and SCE as reference electrode. Results of EIS measurements in the form of Bode plots are presented in Figure 14. For example, in measuring impedance of Ag/AgCl electrodes, two Ag/AgCl electrodes were used, one as working and the other as counter electrode. A 20mV perturbation was applied from 100 kHz to 10 mHz. Measurements were made at ambient temperature around 22±2°C.

Figure 14

In summary, the Ag/AgCl electrodes exhibit the lowest level of impedance and lack of capacitive behaviour. Given the acceptable level of σI and σE (Figure 14), the Ag/AgCl electrode is recommended as a low-noise and low-impedance reference electrode for the measurement of electrochemical noise in the field when using in either the single substrate or NOCS electrode arrangement.

3.4 Case study with polymer coated test subjects; comparison of ENM with DC resistance and EIS

The final section of this study implements the collective knowledge regarding the best suitable PRE for the measurement of polymer coated metal specimens to assess how the results compare to other well-established assessment techniques. Ionic resistance (also known as electrolytic resistance) of a coating remains the most trusted method of assessing the level of protection against corrosion that is afforded by the coating [57]. The values of impedance obtained by EIS, DC resistance (DCR) and ENM techniques have been shown to correspond to the ionic resistance of the coating. ENM, in particular, has been proven to be a sensitive technique for detection and evaluation of defects in organic coatings [58–61]. Herein, the DCR and EIS are utilised as verification techniques. These methods have been previously employed in a large body of literature as complementary test methods to ENM [6,12,19,62–64]. Herein two coating systems with high and medium impedance values have been examined using ENM, EIS and DC resistance methods and results are presented in Figures 15 and 16. The EN data in time domain after DC trend removal are given in supplementary

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materials in Figures S12-S15. The ENM was conducted using both the SCE as a laboratory standard RE and the Ag/AgCl as PRE in Single Substrate electrode configuration in 3% NaCl electrolyte. EIS, ENM (with SCE) and DCR measurements were first conducted in glass cells affixed to the coating surface via rubber O ring and pinch clamps. Then the glass cells were removed and replaced with sandwiched pads of filter paper (saturated with 3% NaCl solution) and Ag/AgCl electrodes. Experimental setups have been shown schematically in Fig. 15.

These results show a very good agreement between the impedance measurements by standard arrangements and the measurement by Ag/AgCl PRE in single substrate mode. The σE for these specimens ranged between 1.6×10^{-5} to 2.1×10^{-4} V (statistical analysis in Figs. S12-S15) that is higher than the intrinsic σE generated by the SCE and Ag/AgCl (0.035 cm^2) electrodes (see Fig. 12). The σI ranged between 8.1×10^{-14} to 1.9×10^{-13} A. That is lower than the intrinsic noise generated by either electrode. However, the effective current noise power from the SCE and Ag/AgCl that is recorded by the circuit would be far lower due to the attenuation by the coating's impedance.

Figure 15

Figure 16

Organic coatings are inherently inhomogeneous in nature which results in a variation of ionic resistance across the coating surface [65]. This further reduces the chance of finding two symmetrical working electrodes, particularly, when working with unknown values in the field. Therefore, future studies on asymmetrical electrodes are needed in order to further enable ENM as a reliable method of assessing organic coatings in the field.

4. CONCLUSIONS

The suitability of a range of pseudo-reference electrodes for fieldwork has been investigated through the measurement of the voltage noise, current noise and the impedance of electrodes.

It is suggested that the three values (average voltage, voltage drift, voltage noise) go a long way towards indicating the "quality" of the electrode in terms of its applicability for use in the assessment of organically coated substrates. Hence the average voltage value should be consistent between electrodes (e.g. no more than 10mV different in the case of silver electrodes in 3% NaCl at 22 °C). Drift from the electrode over each of the twenty-five-minute periods should be low (preferably less than 10mV). In addition, voltage noise should be low (of the order of tens of microvolts or less). This is further complimented by the parameters of current noise and impedance. These should be as low as possible. The maximum acceptable values of these parameters will depend on the application.

Another conclusion is that area of electrode needs be chosen such that it has low impedance (characteristic of larger area) but at the same time has minimum noise (characteristic of smaller area). Regarding the "best" PRE, the results suggest that the Ag/AgCl electrode is the most satisfactory to use when in contact with NaCl solution, exhibiting minimum voltage noise, current noise and impedance. Other electrodes (platinum, copper/copper sulphate) might be used for convenience and would not be ruled out on the basis of this work. Care would be needed in making the choice. For example, platinum electrodes have high impedance and generate some significant noise at 2 cm^2 making them unsuitable particularly for measuring relatively low impedance, e.g. $< 1 \times 10^6$ Ω.cm^2, systems. Cu/CuSO$_4$ electrodes (at least those tested here) generate significant intrinsic noise, making them less suitable for measuring high impedance systems where the current noise levels in particular tend to be very low.

Acknowledgements

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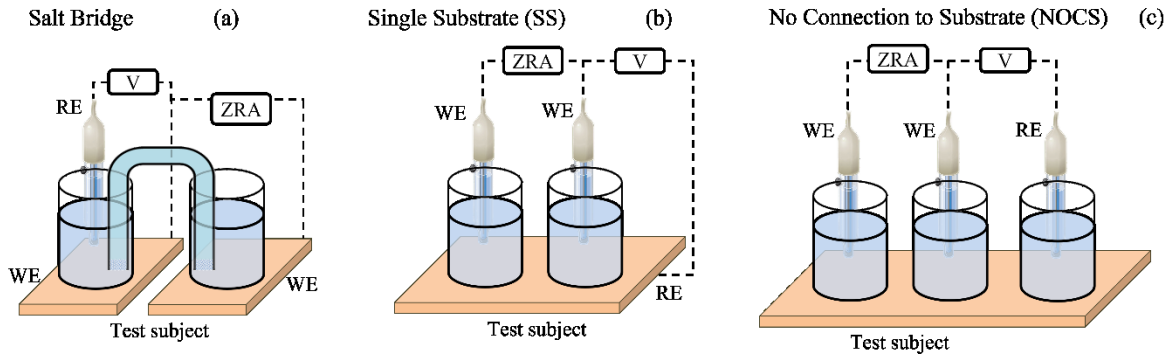
Figure 1 Schematic representation of ENM electrode arrangements for (a) standard salt bridge, (b) single substrate, and (c) no connection to substrate (NOCS) arrangements.
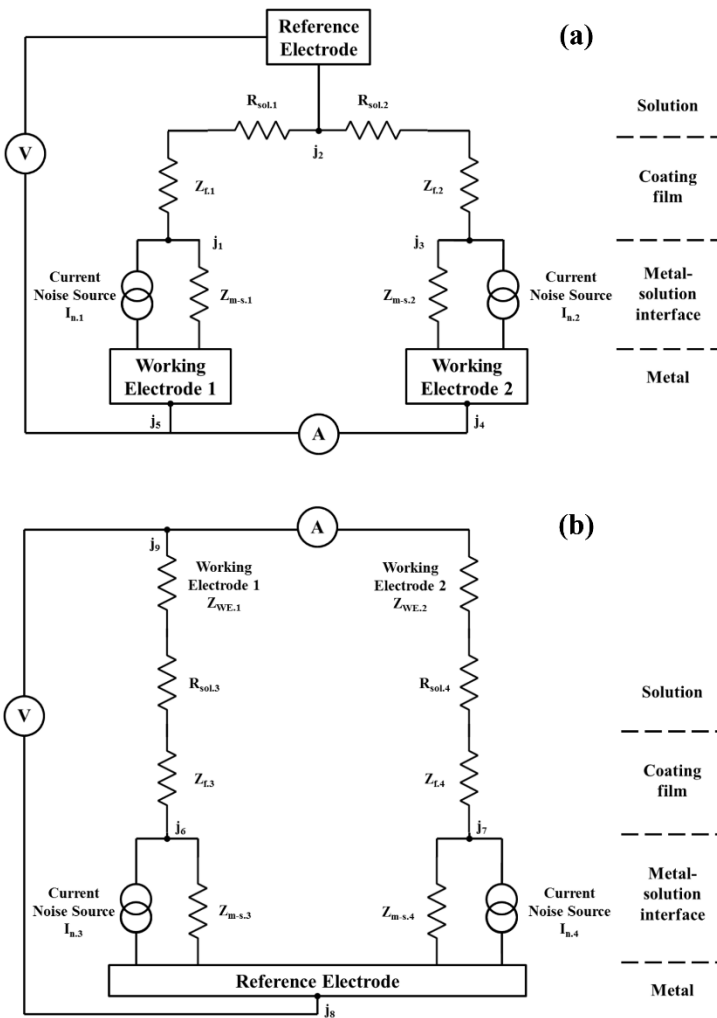
Figure 2 Equivalent electrical circuit diagrams for (a) salt bridge [35] and (b) single substrate (SS) [10] electrode arrangements used in electrochemical noise measurement on a coated substrate.
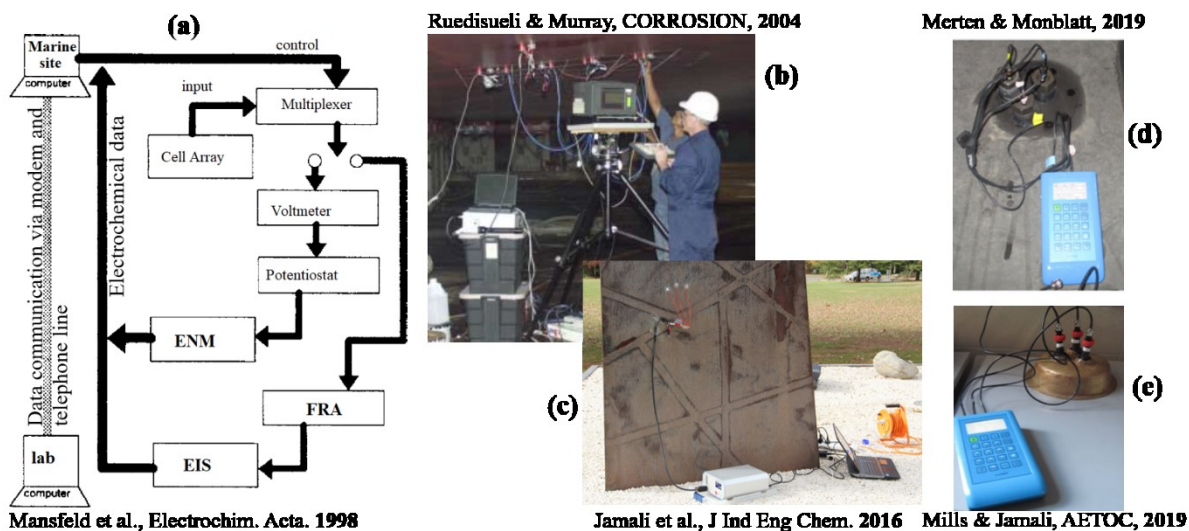
Figure 3 Evolution of ENM application for remote site investigation via (a) modem/telephone line communication [48], (b & c) electric generators [1,45], and (d & e) portable EN analyser "ProCoMeter" [52]. (e) shows ENM on preservation coating on an ancient brass bowl using NOCS arrangement by Ag/AgCl pseudo reference electrodes at the Maritime Museum of Gdansk, Poland.
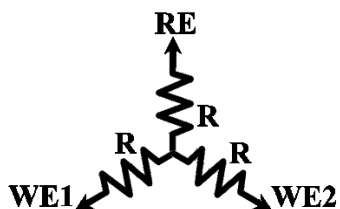
Figure 4 Dummy cell comprised of three identical resistors in star configuration for the examination of instrumental noise.
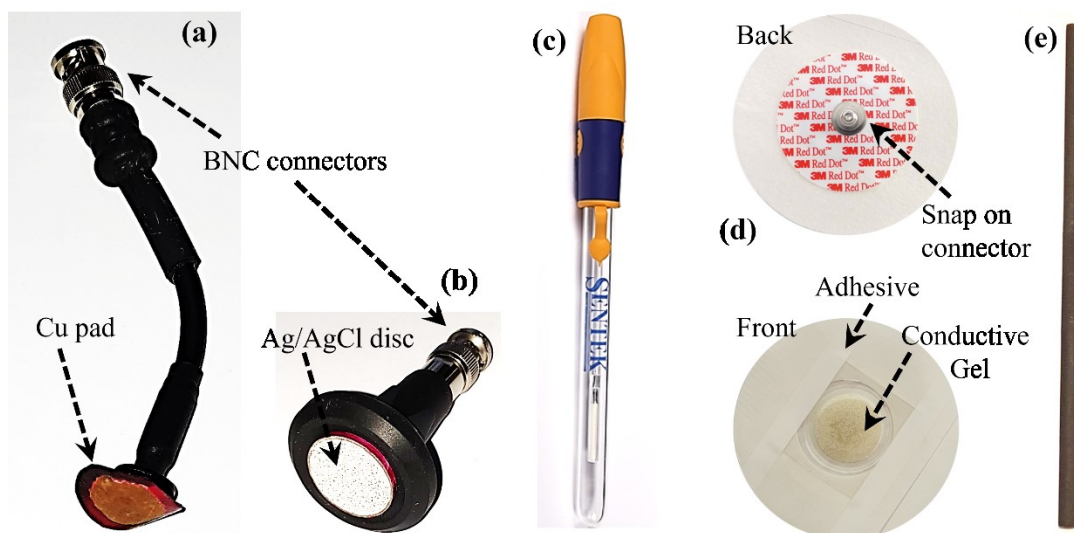
Figure 5 Photograph of (a) Cu pad, (b) Ag/AgCl, (c) SCE, (d) ECG, and (e) carbon reference and pseudo-reference electrodes.
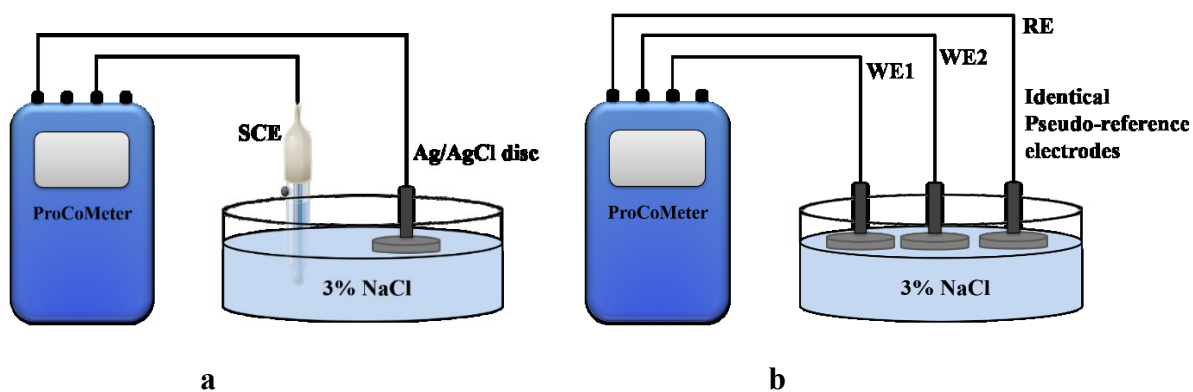
Figure 6 Experimental set-up for measuring (a) the voltage stability and (b) the intrinsic electrochemical voltage and current noise level of pseudo reference electrodes.
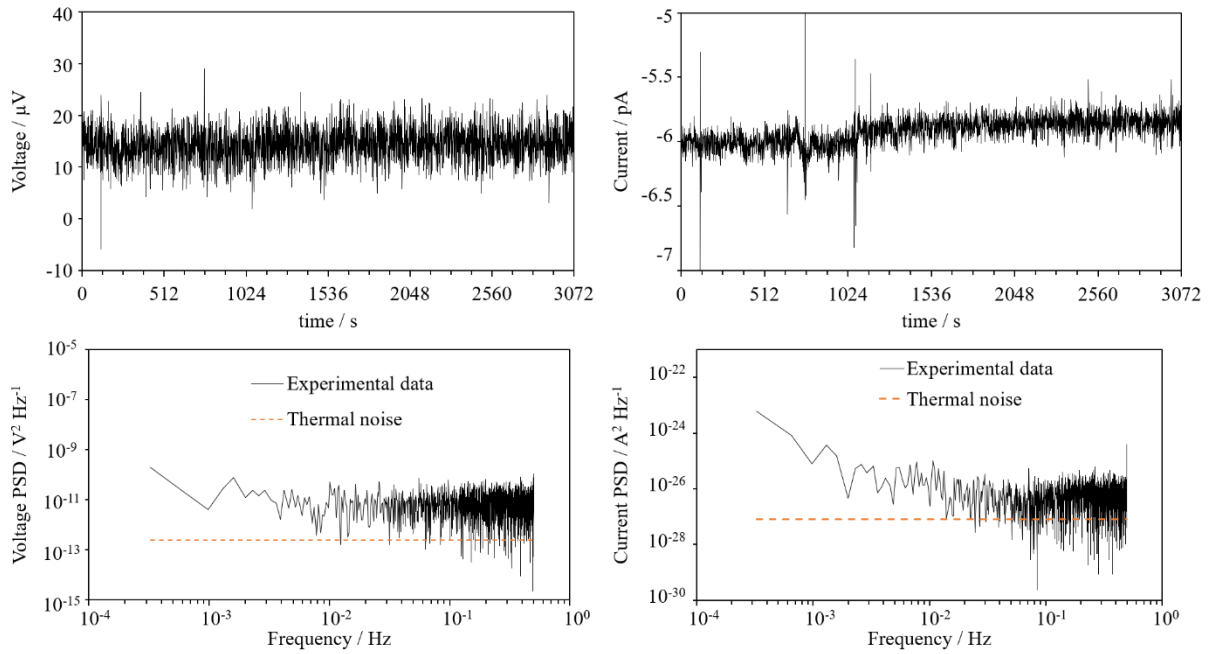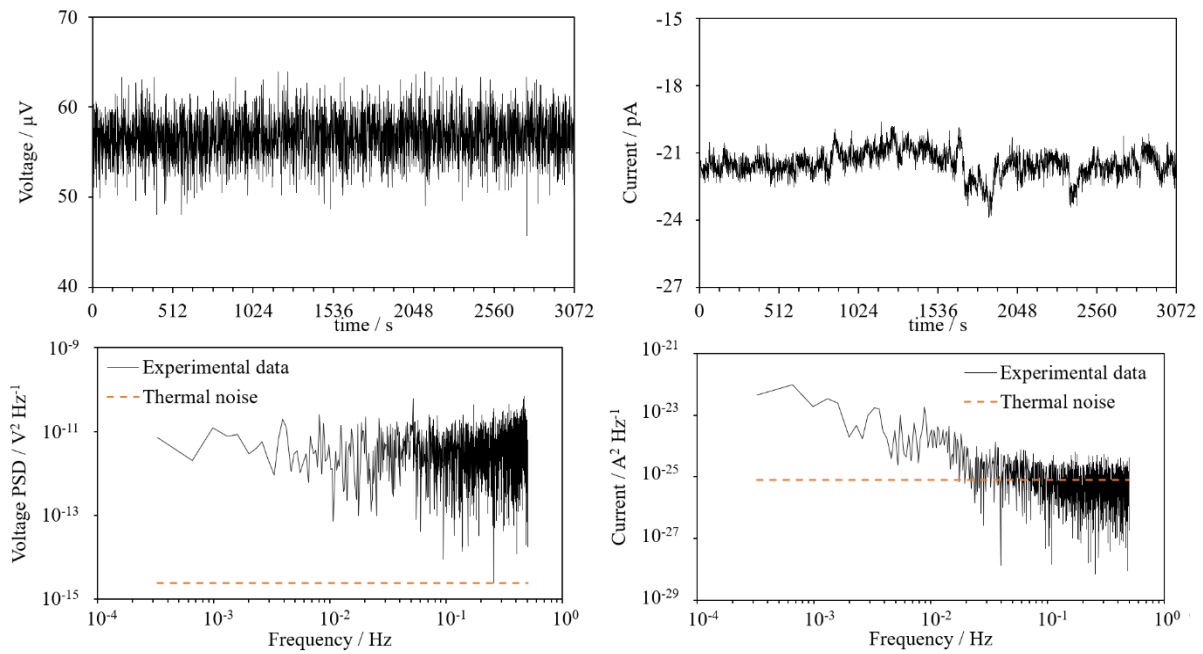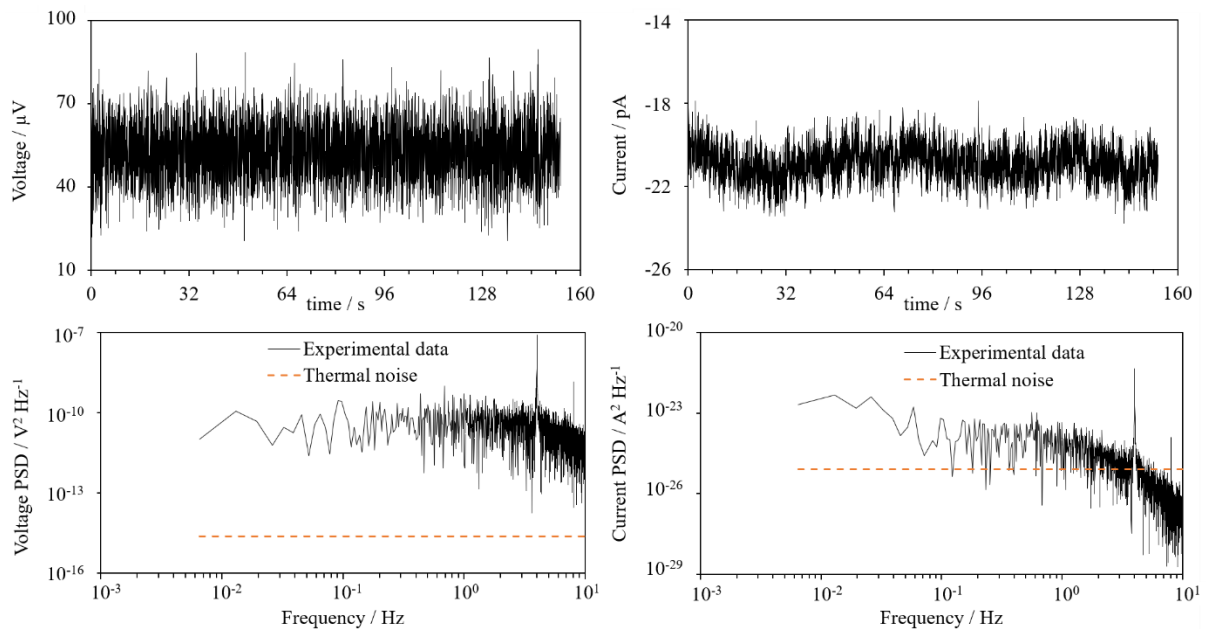
Figure 7 Instrumental noise in the form of time records of (a) potential and (b) current and PSDs of (c) potential and (d) current and comparison to the theoretical thermal noise level of the 10 Mohms resistors in the dummy cell. 3072 data points were collected at 1Hz sampling rate.
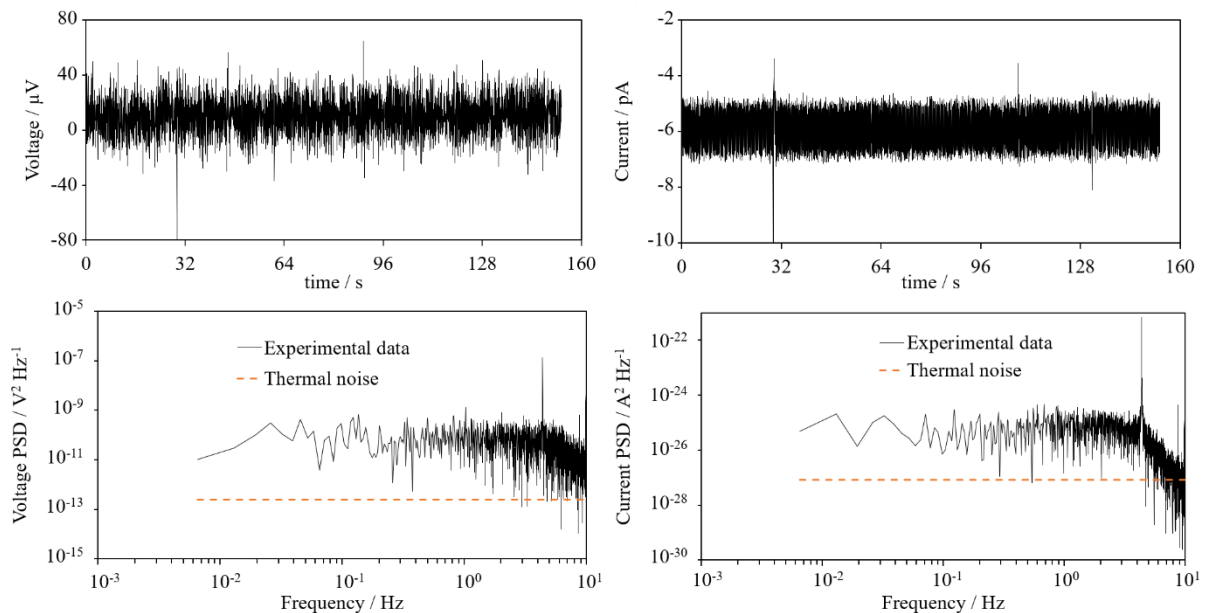
Figure 8 Instrumental noise in the form of time records of (a) Potential and (b) current and PSDs of (c) potential and (d) current and comparison to the theoretical thermal noise level of 10MΩ resistors. 3072 data points were collected at 20Hz sampling rate.

Figure 9 Instrumental noise in the form of time records of (a) Potential and (b) current and PSDs of (c) potential and (d) current and comparison to the theoretical thermal noise level of 100kΩ resistors. 3072 data points were collected at 1Hz sampling rate.

Figure 10 Instrumental noise in the form of time records of (a) Potential and (b) current and PSDs of (c) potential and (d) current and comparison to the theoretical thermal noise level of 100kΩ resistors. 3072 data points were collected at 20Hz sampling rate.
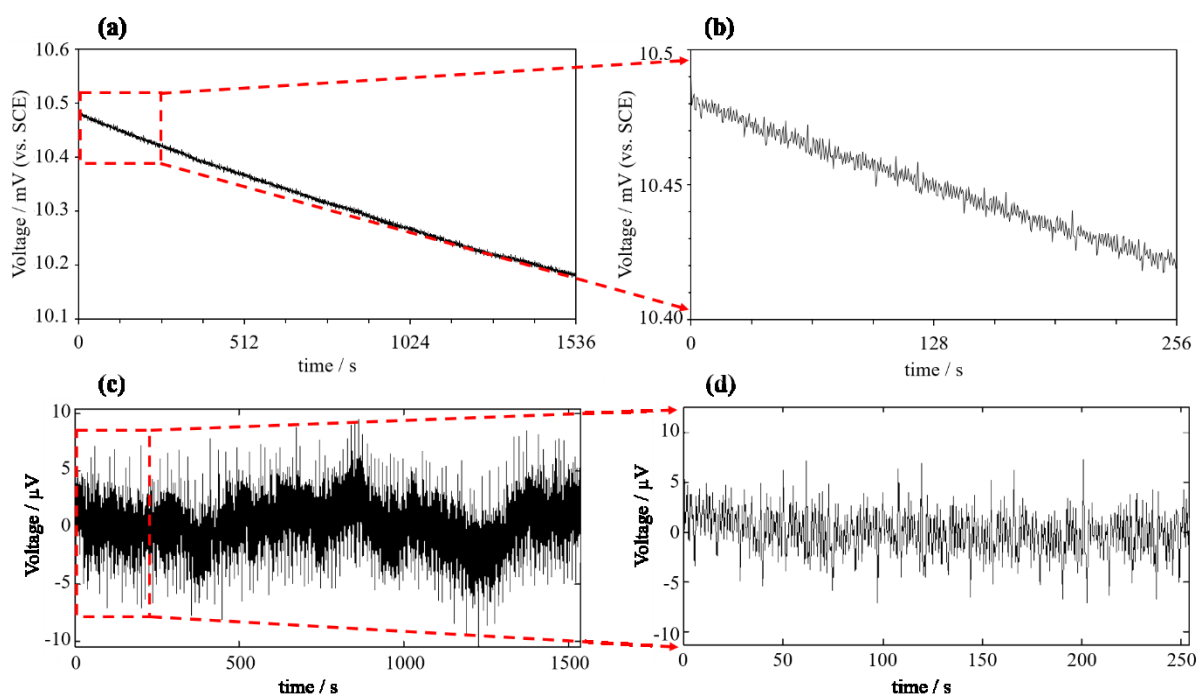
Figure 11 Voltage stability test (VST) results for an Ag/AgCl disc electrode with 4.15cm^2 surface area over 3072 data points sampled at 2Hz frequency. (a) and (b) present the raw data and (c) and (d) present data after polynomial DC detrend. (b) and (d) are the magnified first 512 data points from (a) and (c), respectively.
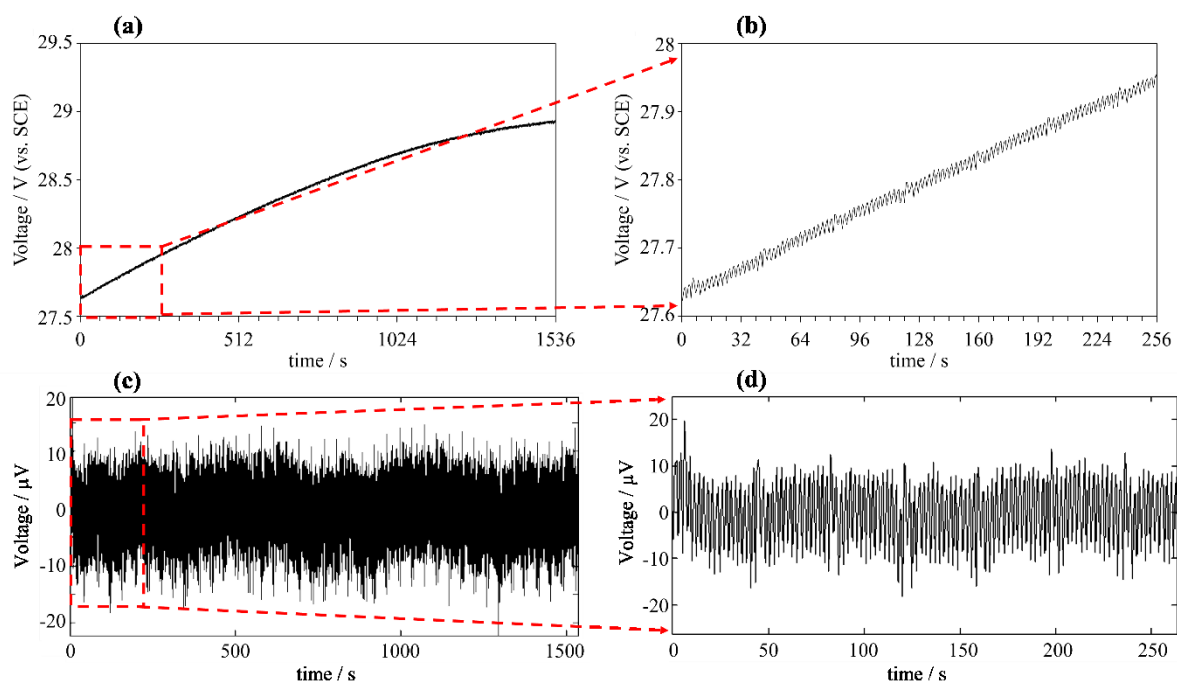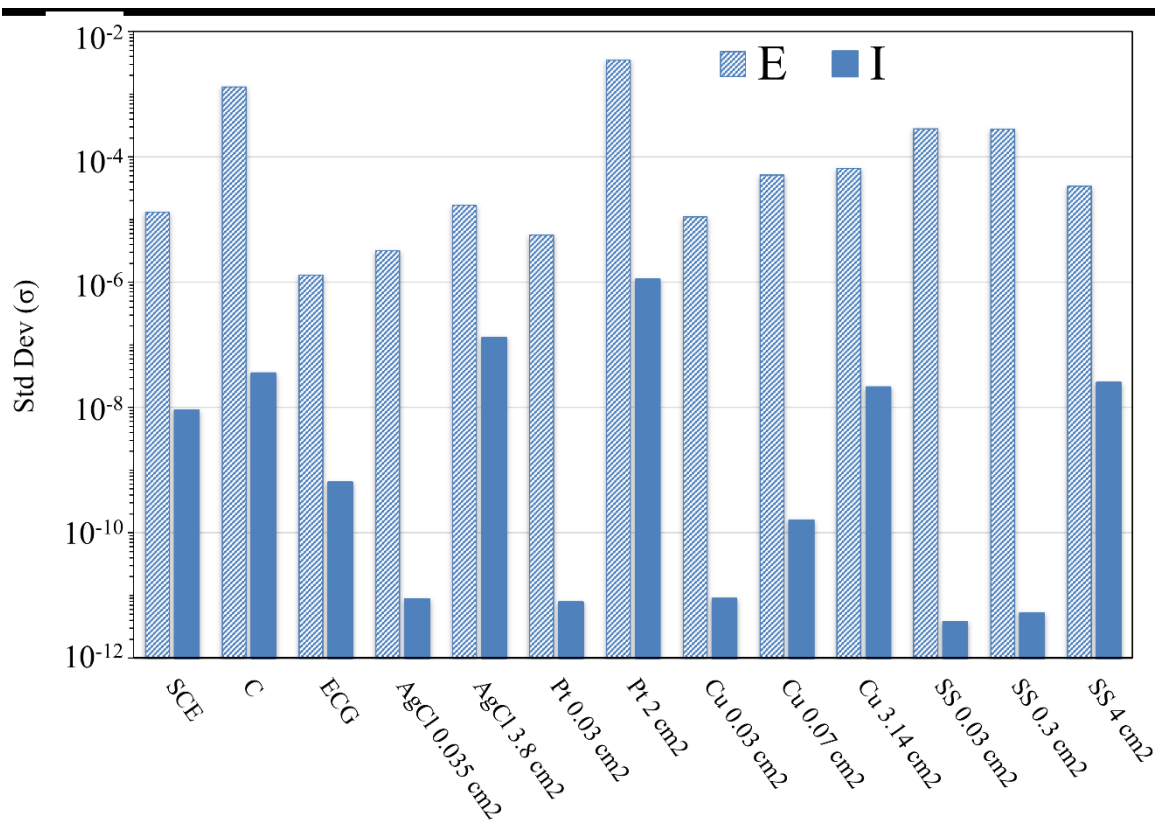

Figure 12 Voltage stability test (VST) results for a Cu disc electrode with 3.2cm^2 surface area over 3072 data points sampled at 2Hz frequency. (a) and (b) present the raw data and (c)

and (d) present data after polynomial DC detrend. (b) and (d) are the magnified first 512 data points from (a) and (c), respectively.

Figure 13: Plot of voltage noise and current noise measured for a variety of electrodes, some with differing area.
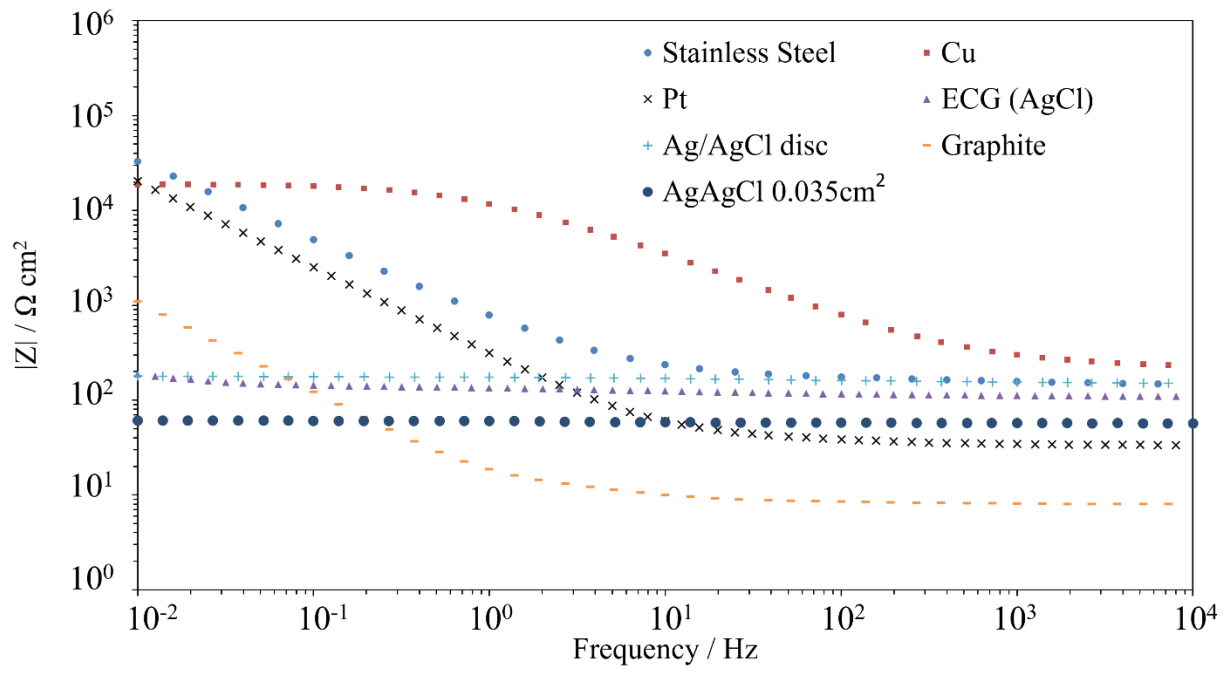
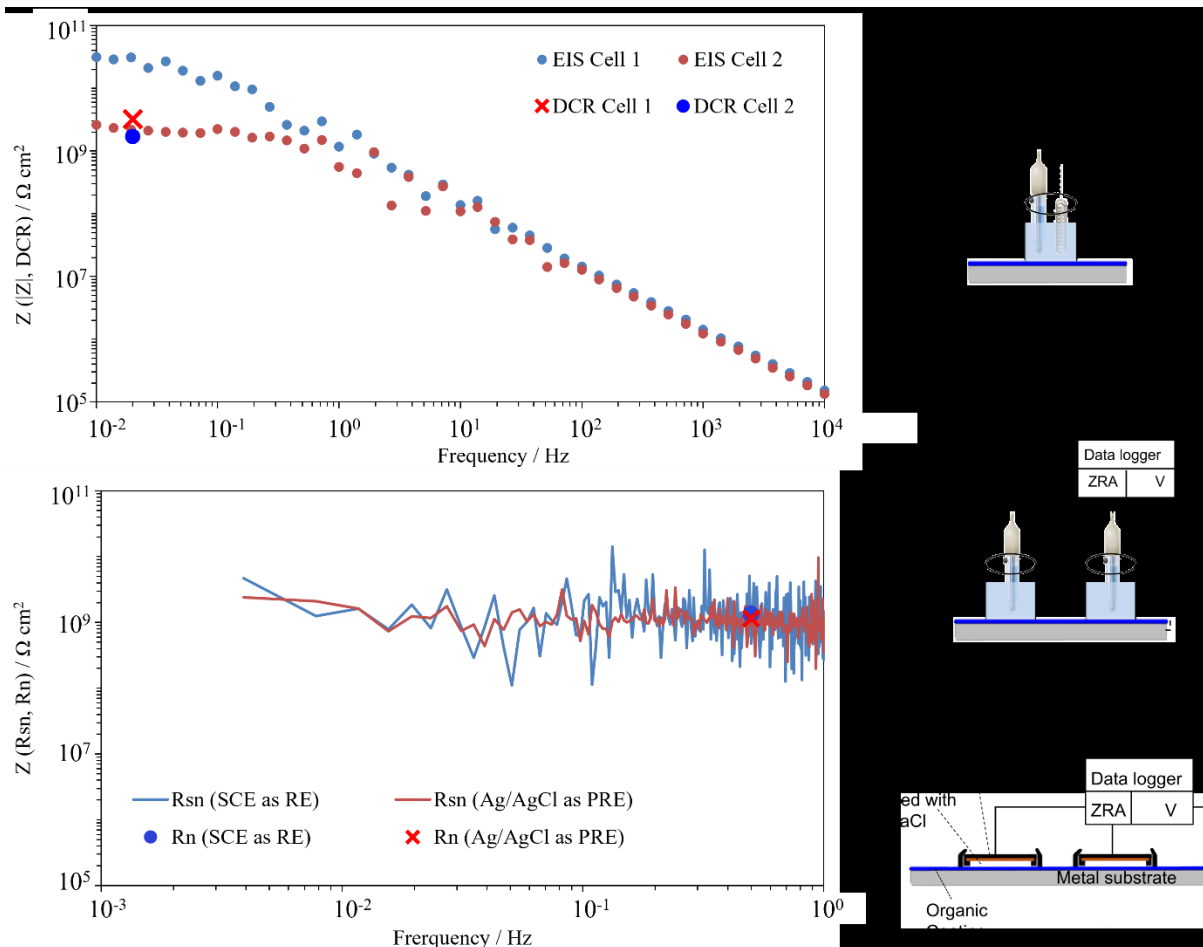**Figure 14** Bode plots comparing the impedance values for the PREs.

Figure 15 Impedance measurements of an epoxy coated steel substrate using EIS, DCR, and ENM methods.
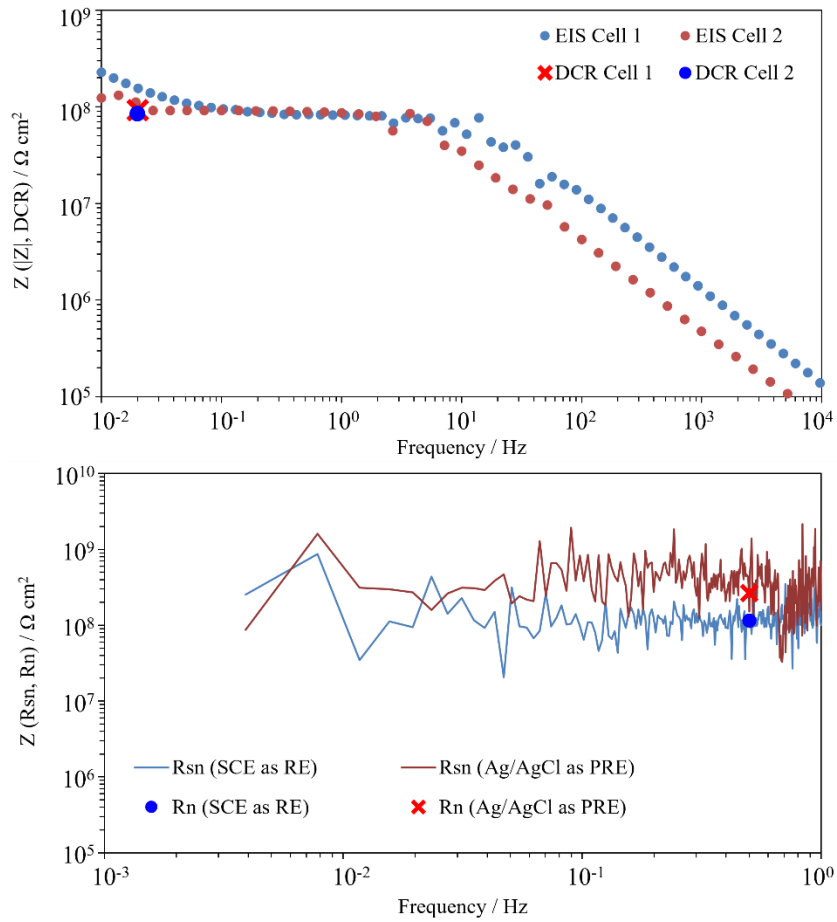
Figure 16 Impedance measurements of a polyurethane coated steel substrate using EIS, DCR, and ENM methods.